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Critical Magnetic Transition in TbNi$_2$Mn –
Magnetization and Mössbauer Spectroscopy

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Abstract: The structural and magnetic properties of the TbNi$_2$Mn$_x$ series (0.9 $\leq$ $x$ $\leq$ 1.10) have been investigated using x-ray diffraction, field- and temperature-dependent ac magnetic susceptibility, DC magnetization (5-340 K; 0-5 T) and $^{57}$Fe Mössbauer spectroscopy (5-300 K). TbNi$_2$Mn$_x$ crystallize in the MgCu$_2$-type structure (space group $Fd-3m$). The additional contributions to the magnetic energy terms from transition metal-transition metal interactions (T-T) and rare earth-transition metal interactions (R-T) in RNi$_2$Mn contribute to their increased magnetic ordering temperatures compared with RNi$_2$ and RMn$_2$. Both the lattice constant $a$ and the Curie temperature $T_C$ exhibit maximal values at the $x$=1 composition indicating strong magnetostructural coupling. Analyses of the ac magnetic susceptibility and DC magnetization data of TbNi$_2$Mn around the Curie temperature $T_C$=147 K confirm the magnetic transition is second order with critical exponents $\beta$=0.77±0.12, $\gamma$=1.09±0.07 and $\delta$=2.51±0.06. These exponents establish that the magnetic interactions in TbNi$_2$Mn are long range despite mixed occupancies of Tb and Mn atoms at the 8a site and vacancies. The magnetic entropy $-\Delta S_M$ around $T_C$ is proportional to $(\mu_0 H/T_C)^{2/3}$ in agreement with the critical magnetic analyses. Mössbauer spectra above $T_C$ are fitted by two
subspectra in agreement with refinement of the x-ray data while below $T_c$ three sub-spectra are required to represent the three inequivalent local magnetic environments.

**Key Words:** Rare earth metals and alloys, magnetic phase transition, magnetization, magnetic susceptibility, Mössbauer spectroscopy

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1. Introduction

Interest in rare earth–transition metal (R-T) intermetallic compounds has continued unabated in recent years due in part to their continuing technological importance and potential applications [e.g. 1, 2]. Compounds rich in the rare earths have attracted interest as several series exhibit a large magnetocaloric effect [e.g. 3]. Compounds of rare earths with Mn such as RMn$_2$X$_2$ (X=Ge or Si) [4] and RMn$_2$ [5] are of particular interest due to interplay between the 3d and 4f magnetism and the sensitive dependence of the Mn moment and sublattice structures on Mn-Mn interatomic distances. In the RMn$_2$ system for example, there is a critical Mn-Mn spacing $d_{\text{Mn-Mn}}$ ($\sim 2.66$ Å) below which the Mn moments become unstable [5]. Substitution of a third element for Mn can lead to significant modification of the magnetic properties leading to the development of materials with interesting magnetic and physical properties [e.g. 2, 6, 7].

RNi$_2$Mn compounds with R=Tb, Dy, Ho, and Er have been reported to crystallize in the MgCu$_2$-type structure of space group $Fd-3m$ with TbNi$_2$Mn found to exhibit the largest magnetic ordering temperature $T_C$ [8, 9]. For TbNi$_2$Mn, Wang et al. [9] reported mixed occupancies of Ni (74%) and Mn (26%) at the 16d sites with mixed occupancies of Tb (74%) and Mn (22%) at the 8a site together with 4% vacant 8a sites. Jackson et al. [10] also reported that TbNi$_2$Mn has the MgCu$_2$-structure, although Mushnikov et al. [11] concluded that the crystal structure of TbNi$_2$Mn is described by the AuBe$_5$-type structure of space group $F4-3m$. Table I lists the main preparation conditions for these TbNi$_2$Mn samples along with structural information and magnetic transition temperatures. It is interesting to note that despite the nominal compositional equivalence and similarities in heat treatments, the TbNi$_2$Mn samples exhibit lattice parameters ranging from 7.123 Å [10] to 7.184 Å [11] with Curie temperatures ranging from $T_C \sim 131$ K [9] to $T_C \sim 151$ K [10]. The high vapour pressure of Mn (leading to possible variations in the nominal Mn composition under different preparation and heat treatment conditions), together with the sensitive dependence of the Mn magnetism on Mn-Mn interatomic distances [5-7] is likely to contribute to the observed range.
in properties. Moreover, RNi$_2$Mn has been found to exhibit considerably higher Curie temperatures than the corresponding isostructural compounds RNi$_2$ and RMn$_2$ [9]. TbNi$_2$Mn, has been found to exhibit the highest Curie temperature with reported values in the range $T_C$~140(±10) K (Table I) compared with $T_C$~37.5 K and $T_C$~54 K for TbNi$_2$ and TbMn$_2$, respectively [9].

In order to clarify the factors that contribute to the range of structural and magnetic properties reported for TbNi$_2$Mn (Table I), we have carried out a systematic investigation of a series of TbNi$_2$Mn$_x$ compounds ($0.9 \leq x \leq 1.10$) prepared in the same manner. A further aim of the present work is therefore to clarify the magnetic interactions occurring in TbNi$_2$Mn compared with TbNi$_2$ and TbMn$_2$ to account for this increased Curie temperature. The samples have been investigated by x-ray and neutron diffraction, DC magnetization, ac susceptibility (5-340 K) and Mössbauer spectroscopy (5-300 K). Critical exponent analyses have been applied successfully to investigate the magnetic behaviour of a wide range of materials (e.g. La$_{1-x}$Ca$_x$MnO$_3$ [12], TbCo$_2$ and TbCo$_{1.9}$Fe$_{0.1}$, [13], R$_{1-x}$A$_x$MnO$_3$ (divalent cation A), La$_{0.73}$Ba$_{0.27}$MnO$_3$, Tl$_2$Mn$_2$O$_7$, Ni-Mn-Ga and CeFe$_2$-related compounds [14-17]); here we apply a similar approach in detailed critical analyses of the magnetic phase transition at $T_C$ in TbNi$_2$Mn.

2. Experimental

The TbNi$_2$Mn$_x$ ($x=0.90, 0.97, 1.00, 1.03$ and $1.10$), Tb$_{1-y}$Ni$_2$ ($y=0.00, 0.02$ and $0.05$) and TbMn$_2$ samples were prepared using starting elements of purities $\geq 99.9\%$. Ingots of mass $\sim$ 2 g were prepared at UNSW@ADFA by standard argon arc-melting procedures with each ingot melted at least five times for improved homogeneity. The TbNi$_2$Mn($^{57}$Fe) sample for the Mössbauer study was prepared from an ingot doped with $\leq 0.5$ wt% $^{57}$Fe. We have also investigated the behaviour of an $\sim$8 g TbNi$_2$Mn sample (identified as TbNi$_2$Mn*). This relatively large sample was prepared at the Institute of Physics, Beijing in a similar manner (argon arc melting with five melts for improved homogeneity) for forthcoming neutron diffraction experiments. All samples, which have been
studied in the as-prepared state, were characterized by x-ray diffraction (CuKα radiation; λ = 1.5418 Å). The structure of the TbNi$_2$Mn$^*$ sample was further checked by neutron diffraction at 300 K (high intensity diffractometer Wombat, OPAL, Lucas Heights; λ = 2.4072 Å) for comparison with the x-ray diffraction data. Magnetization measurements were carried out over the temperature range 5-340 K in a SQUID magnetometer ($\mu_0H = 0-5$ T). The DC field dependences of the magnetic ac susceptibility were recorded using a conventional physical properties measurement system (PPMS-9, Quantum Design, $\mu_0H = 0 - 8$ T) over the temperature range 5–340 K. The $^{57}$Fe Mössbauer spectra were obtained between 5 K and 300 K using a standard constant-acceleration spectrometer and a $^{57}$CoRh source. The spectrometer was calibrated at room temperature with an α-iron foil.

3. Results and Discussion

3.1 Structural Properties

Figure 1(a) shows the X-ray diffraction patterns of the set of five TbNi$_2$Mn$_x$ samples (x= 0.90, 0.97, 1.00, 1.03 and 1.10) studied in the as-prepared state. All samples can be indexed with the MgCu$_2$-type structure ($Fd-3m$) in which Cu are located at the 16d site and Mg at the 8a site [5, 8]. A small impurity phase <2 % (reflections around 2θ∼29°) is observed, as in the case of HoNi$_2$Mn and ErNi$_2$Mn [9]. The skewing of the high angle peaks indicates the presence of large strains in these un-annealed samples. As discussed below, it is noted that the (200) reflection of space group ($F4-3m$) [11] is absent for all TbNi$_2$Mn$_x$ samples of Fig. 1(a). The lattice constants were derived using the Le Bail method with a maximum indicated around Mn composition x~1.0 (Fig. 2 (a)). Similar behaviour has been detected in ErNi$_2$Mn$_x$ [18].

Mushnikov et al. [11] observed additional (200) and (420) reflections in the room temperature and 4.2 K neutron diffraction patterns of TbNi$_2$Mn annealed at 870°C for 7 days. They concluded that the crystal structure of TbNi$_2$Mn is described by the AuBe$_5$-type structure of space group $F4-3m$, a superstructure of $Fd-3m$. It should be noted that a (200) peak can also be discerned with CuKα
radiation for a TbNi$_2$Mn sample annealed at 750°C for 7 days [9] and with CrK$_\alpha$ radiation for TbNi$_2$Mn annealed at 870°C for 7 days [11]. On the other hand a (200) peak is not observed with CrK$_\alpha$ radiation for their other TbNi$_2$Mn$_x$ samples with x=0.25, 0.50 and 0.75 annealed at 870°C for 7 days [20]. Given the absence of the (200) reflection in the present as-prepared TbNi$_2$Mn$_x$ samples which exhibit the MgCu$_2$-type structure, it is clear that the final structure adopted by TbNi$_2$Mn$_x$ compounds depends sensitively on the preparation conditions, the Mn composition and sample heat treatments. The MgCu$_2$-type structure is obtained for random distributions of Tb and Mn in the 8a site and Ni and Mn in the 16d site [9], whereas site ordering leads to the AuBe$_5$-type structure with Tb in the 4c site and Tb and Mn in the 4a site and Ni and Mn distributed in the 16e site [11]. The occurrence of vacancies is also likely to influence the structure: while 4% of vacant 8a sites were reported for the MgCu$_2$-type structure for TbNi$_2$Mn [9], optimal refinements to the AuBe$_5$-type structure resulted in the off-stoichiometric composition TbNi$_{2.09}$Mn$_{0.81}$ with the introduction of vacancies leading to increase in refinements agreement values [11]. Similar behaviour - with sensitive dependence of the structure on composition and sample preparation conditions – has also been exhibited by the RNi$_2$ system [21] where a temperature induced phase transition (and pressure-induced transition for YNi$_2$) is detected from $F4\bar{3}m$ to $Fd\bar{3}m$ [21]. A full crystallographic investigation of the conditions under which the different structures are obtained for TbNi$_2$Mn – MgCu$_2$-type or AuBe$_5$-type – and the factors governing the transformation from one structure to the other is required.

The room temperature neutron diffraction pattern for TbNi$_2$Mn* sample is shown in Fig. 1(b). Since the neutron-scattering lengths of Tb, Ni, and Mn atoms are substantially different [11], the neutron pattern is expected to demonstrate more clearly the differences between space groups $Fd\bar{3}m$ and $F4\bar{3}m$ as mentioned in [11] via, for example, the presence or absence of reflections such as (200) and (420). As expected on the basis of our X-ray diffraction patterns (Fig. 1(a)), the neutron diffraction pattern of as-prepared TbNi$_2$Mn* (Fig. 1(b)) exhibits the MgCu$_2$-type structure with no
evidence of the (200) and (420) reflections of the AuBe$_3$-type structure [11]. Rietveld refinement of the room temperature neutron diffraction pattern (well above the magnetic-ordering temperature of TbNi$_2$Mn* $\sim$147 K as discussed below), confirms that the space group of the as-prepared TbNi$_2$Mn* sample is $Fd\bar{3}m$. The quality of fit parameters are: pattern factor, $R_p$=3.24% weighted pattern factor, $R_w$=4.23% and the expected pattern factor $R_{exp}$=0.53%.

3.2 Magnetic Behaviour

The magnetic behaviour of all TbNi$_2$Mn$_x$ samples (x= 0.90, 0.97, 1.00, 1.03 and 1.10) have been investigated. Given the $\sim$8 g available for the as-prepared TbNi$_2$Mn* sample, we chose to investigate this sample in detail to ensure consistency for measurements using the variety of magnetic methods.

Fig. 3 (a) shows the temperature dependences of the low field DC magnetization ($\mu_0H$=0.005 T) for TbNi$_2$Mn* on warming and cooling after first cooling in zero field (ZFC). The Curie temperatures $T_C^{DC}$ for all TbNi$_2$Mn$_x$ samples were determined as the temperature at which the $dM/dT$ versus $T$ curve exhibits a minimum (e.g. inset to Fig. 3(a)). The $T_C$ values for the set of TbNi$_2$Mn$_x$ samples (Fig. 2(b)) exhibit a similar dependence on Mn composition as the lattice parameter $a$ (Fig. 2(a)) with a maximum around $x$=1.0. The compositional dependences of $a$ and $T_C$ indicate that the distance of separation of Mn atoms plays a critical role in governing the magnetic behaviour of TbNi$_2$Mn$_x$.

The changes in transition temperature resulting from a change in the unit cell volume due to the variation of Mn composition can be estimated from recent pressure studies of TbNi$_2$Mn [10]. Assuming that values of, $B_0$, the bulk modulus and, $dT_C/dP$, the rate of change of transition temperature with pressure $P$, do not change significantly with Mn composition in TbNi$_2$Mn$_x$, and using $B_0$=128 GPa and $dT_C/dP$ = -1.96 K/GPa for TbNi$_2$Mn [10], the change of $T_C$ with $x$=1.0 (unit
cell volume \( V = 373.5 \, \text{Å}^3 \), compared with \( x = 0.9 \) \((V = 365.4 \, \text{Å}^3)\), is estimated as \( \Delta T_C \approx 5.4 \, \text{K} \). This calculated change in the critical temperature - based solely on the volume change of \( \Delta V/V = 2.17\% \) from \( \text{TbNi}_2\text{Mn}_{0.9} \) to \( \text{TbNi}_2\text{Mn}_{1.0} \) – compares well with the experimentally measured difference of \( \Delta T_C \approx 7 \pm 1 \, \text{K} \). (Fig. 2(b)) and confirms the occurrence of strong magnetostructural coupling in \( \text{TbNi}_2\text{Mn}_x \).

For a given set of preparation conditions, differences in \( T_C \) values for \( \text{TbNi}_2\text{Mn}_x \) (Table I) are concluded to be due mainly to both the concentration of Mn atoms and chemical pressure effects related to variations in the spacing between magnetic atoms. This is evident in the case of \( \text{TbNi}_2\text{Mn} \) for which \( T_C^{\text{DC}} = 148 \pm 2 \, \text{K} \) for the present \( \text{TbNi}_2\text{Mn}^* \) sample (Fig 3(a)) compared with \( T_C = 151 \, \text{K} \) [10], \( T_C = 131 \, \text{K} \) [9] and \( T_C = 142 \, \text{K} \) [11]. Just as variations in the sample compositions and preparation conditions alter the structural behaviour of \( \text{TbNi}_2\text{Mn} \) as discussed above, these effects account for the observed spread in \( T_C \) values (Table I).

Independent of the \( T_C \) value for a particular sample, a key feature in the magnetism of \( \text{TbNi}_2\text{Mn} \) compared with \( \text{TbNi}_2 \) and \( \text{TbMn}_2 \), is the significantly higher transition temperature exhibited by \( \text{TbNi}_2\text{Mn} \) \((T_C \sim 140(10) \, \text{K})\) compared with those of \( \text{TbNi}_2 \) \((T_C \sim 37.5 \, \text{K})\) and \( \text{TbMn}_2 \) \((T_C \sim 54 \, \text{K})\) [9, 21, 22]. Fig 3(c) shows a graph of \( T_C \) values versus the de Gennes factor, \( G_R = (g-1)^2J(J+1) \), for \( \text{RNi}_2\text{Mn} \) [9], \( \text{RNi}_2 \) [22, 23] and \( \text{RMn}_2 \) [24]. There are three exchange interactions in \( \text{R-T} \) compounds: indirect \( \text{R-R} \) interactions, indirect \( \text{R-T} \) interactions, and direct \( \text{T-T} \) interactions. According to a molecular field approximation, the Curie temperature \( T_C \) in \( \text{R-T} \) compounds can be expressed by [25, 26]:

\[
T_C = \frac{T_{T-T} + T_{R-R} + \sqrt{(T_{T-T} - T_{R-R})^2 + 4T_{R-T}^2}}{2},
\]

where \( T_{T-T} \), \( T_{R-R} \) and \( T_{R-T} \) represent the contributions to \( T_C \) resulting from the \( \text{T-T} \), \( \text{R-R} \) and \( \text{R-T} \) interactions, respectively. \( T_{T-T} \), \( T_{R-R} \) and \( T_{R-T} \) are given by the microscopic exchange-coupling
parameters $A_{i,j}$ (i, j=R, T) where $T_{R-R} = \frac{2A_{R,R}G_R}{3}$, $T_{R-T} = \frac{2A_{R,T}G_T}{3}$ and $T_{T-T} = \frac{2A_{T,T}G_T}{2}$. Here $Z_{i,j}$ is the number of j atoms nearest the i atom (for the RT$_2$ system, $Z_{R,R}$, $Z_{R,T}$, $Z_{T,R}$ and $Z_{T-T}$ are 4, 12, 6 and 6, respectively [9, 25]) and $G_R$ is the de Gennes factor $(g-1)^2J(J+1)$ for rare earth atoms while $G_T$ is the corresponding de Gennes factor for transition metal atoms [25, 26]. Assuming that Ni does not carry a moment in RNi$_2$ compounds [27] (or carries a small moment e.g. $\mu_{Ni}=0.2 \mu_B$ for GdNi$_2$ [28]), R-T and T-T interactions are very weak or absent and the magnetism in RNi$_2$ is dominated by R-R exchange [27]. For RMn$_2$ the magnetic state of the Mn atoms depends critically on the rare earth element: the Mn moment is small in RMn$_2$ with R=Dy, Ho and Er while the Mn moment is estimated to be $\mu_{Mn}=0.25 \mu_B$ in TbMn$_2$ [24]. Moreover, the transition temperatures in RMn$_2$ with R=Gd-Tm are in fairly good agreement with the de Gennes rule [9, 24] indicating that the magnetism is driven primarily by the rare earth element [24]. This is supported by Fig. 3(c) which shows that the transition temperatures $T_C$ for RNi$_2$ and RMn$_2$ exhibit linear relationships with the de Gennes factor $G_R$ and a temperature intercept close to zero for both compounds. The changes in volume which occur in RNi$_2$ and RMn$_2$ for different rare earths also play a role in the strength of the R-R interaction. For example, from R=Tb to R=Er, the fractional changes in unit cell volumes for RNi$_2$ and RMn$_2$ are $\Delta V/V\approx0.15\%$ and $\Delta V/V\approx0.52\%$, respectively [9]. These volume changes lead to differences between the $A_{R,R}$ exchange-coupling parameters which in turn affect the transition temperatures. For example for RNi$_2$ compounds, $A_{Tb-Tb}=2.2\times10^{-23}$ J (~1.6 K) for TbNi$_2$ and $A_{Er-Er}=1.6\times10^{-23}$ J (~1.2 K) for ErNi$_2$ [25].

Fig. 3(c) demonstrates that $T_C$ for RNi$_2$Mn is not predicted by the de Gennes rule alone. Extrapolation of $T_C$ values for RNi$_2$Mn versus $G_R$ leads to an intercept of ~ 26.6 K, indicating a $J_{T-T}$ contribution. Assuming that the $A_{R,R}$ values in RNi$_2$Mn are the same as those deduced from RNi$_2$ compounds of similar unit cell volumes [25], the $T_{Tb-Tb}$ contribution resulting from the $J_{Tb-Tb}$ interaction can be estimated. As examples, for R=Tb and R=Er the unit cell volumes are: $V=366.8$
Å$^3$ for TbNi$_2$Mn and $V=367.1$ Å$^3$ for TbNi$_2$ (c.f. $V=445.1$ Å$^3$ for TbMn$_2$) [9, 22], and $V=361.8$ Å$^3$ for ErNi$_2$Mn and $V=361.6$ Å$^3$ for ErNi$_2$ (c.f. $V=421.9$ Å$^3$ for ErMn$_2$) [9, 22]. Using $T_{R-R} = \frac{2Z_{R}^{2} \mu_{R}^{2} \mu_{G}^{2}}{3}$ this leads to $T_{\text{Tb-Tb}} = 28$ K ($Z_{\text{Tb-Tb}} = 3$ in TbNi$_2$Mn while $Z_{\text{Tb-Tb}} = 4$ in TbNi$_2$). This demonstrates that the $J_{R-T}$ and $J_{T-T}$ components in the magnetic energy terms for RNi$_2$Mn contribute significantly to the increase of magnetic ordering temperatures compared with corresponding RNi$_2$ and RMn$_2$ compounds. This finding is supported by the moment values $\mu_{\text{Ni}} = 0.3(2)$ µ$_{B}$ and $\mu_{\text{Mn}} = 1.4(2)$ µ$_{B}$ determined for TbNi$_2$Mn at 4.2 K [11]. It is concluded that the presence of Ni and Mn magnetic moments in RNi$_2$Mn leads to stronger R-T and T-T exchange interactions, resulting in the higher $T_C$ values for the series of RNi$_2$Mn compounds compared with RNi$_2$ and RMn$_2$. This behaviour agrees well with the general tendency detected in R$_{m}$T$_{n}$ compounds that, with decreasing m/n ratio (i.e. from T-poor to T-rich compounds), the contribution $T_R$ of the R-R interactions to $T_C$ decreases while the T-T and R-T become dominant [25]. Similarly the changes in $T_C$ with Mn composition for TbNi$_2$Mn$_x$ (Fig. 2(b)) are due to variations in the R-T and T-T interactions resulting from the strong magnetostructural coupling and modifications of the Mn magnetic state due to volume changes (similar changes are observed in the RMn$_2$ system [5]).

3.3. Magnetic Transition – Mean Field Analysis

3.3.1 Exponents - AC Magnetic Susceptibility

The ac magnetic susceptibility of TbNi$_2$Mn* in Fig. 3(b) is similar to that reported previously [9]. The Curie temperature $T_C^{ac} = 147\pm 2$ K (minimum of $d\chi/dT$; inset to Fig. 3(b)) agrees well with $T_C^{DC} = 148\pm 2$ K obtained from the DC magnetization measurements of Fig. 3(a). The ac susceptibility data also indicate an extended shoulder as the temperature approaches ~200 K as also reflected by the inflection in $d\chi/dT$ around ~185 K. This feature may be associated with the slight impurity noted above in the x-ray diffraction pattern of Fig 1(a) although its origin remains unclear.
We have analyzed the high field ($\mu_0 H_{DC} > 0.5$ T) ac susceptibility data measured around the Curie temperature (Fig 4) by mean field theory. Application of large DC fields eliminates the ac susceptibility response to technical magnetization effects such as domain walls while suppressing the background [14-16], thereby ensuring that only critical data are analyzed. Figure 4 reveals several features of the ac susceptibility with increasing DC field: (i) the magnitude decreases; (ii) the width of the predominant peak increases and (iii) the position of the broad peak shifts to higher temperatures. The critical behaviour can be derived from the maxima $\chi_M(H, T)$ in the temperature dependence of ac susceptibility $\chi(H, T)$ in DC fields with $T_M$ defined as the temperature of maximum $\chi_M(H, T)$ [14]. According to the conventional static scaling law [14-16, 29, 30 and references therein], the temperature dependence of maxima $\chi_M(H, T)$ is governed by power laws [14-16]:

\[
\chi_M(H, T_M) \propto H^{1/\delta - 1},
\]

\[
\chi_M(H, T_M) \propto ((T_M - T_C)/T_C)^{-\gamma},
\]

\[
(T_M - T_C)/T_C \propto H^{1/\gamma + \beta}.
\]

The exponent $\delta = 2.51 \pm 0.06$ was obtained on fitting equation (2) to a double-logarithmic plot of $\chi_M(H, T_M)$ as a function of DC field (Fig. 5(a)). Following the approach described in [14, 31], we have determined the critical temperature to be $T_C^{\text{crit}} = 147.0 \pm 1.7$ K on extrapolation of the graph of $T_M$ against $(\mu_0 H)^{0.57}$ (Fig. 5(b); equation (4)). This value of $T_C^{\text{crit}} = 147.0 \pm 1.7$ K is in very good agreement with the values $T_C^{\text{DC}} = 148.0 \pm 1$ K and $T_C^{\text{ac}} = 147\pm2$ K determined directly from the magnetization and ac magnetic susceptibility measurements (Figs. 3(a), 3(b) respectively) (as a further check it should be noted that $T_C^{\text{crit}} = 148.4 \pm 1.3$ K was obtained from a graph of $T_M$ versus $(\mu_0 H)^{0.538}$. The exponent value 0.538 is based on $\gamma + \beta = 1.86$ derived below from equation (4)). The agreement between the $T_C$ values determined directly from the magnetization data and from critical
exponent analysis confirms the applicability of the power laws to the TbNi$_2$Mn system. For the remainder of the critical exponent analyses we apply $T_C = 147.0$ K.

Figs. 5(c) and 5(d) are double-logarithmic plots of $\chi_M(H, T_M)$ versus $(T_M - T_C)/T_C$ and $(T_M - T_C)/T_C$ versus $\mu_0 H$ respectively. The high degree of linearity obtained on fitting equations (3) and (4) to Figs. 5(c) and 5(d) indicates that these power laws apply to TbNi$_2$Mn with exponent values of $\gamma = 1.09 \pm 0.07$ and $\gamma + \beta = 1.86 \pm 0.12$, $\beta = 0.77 \pm 0.12$ determined respectively. Description of the critical magnetic behaviour of TbNi$_2$Mn by the above power laws confirms that the transition is second order. However, it should be noted that while the region of reduced temperature $(T_M - T_C)/T_C$ over which equation (3) applies to TbNi$_2$Mn is quite extended (~0.1 to 0.3; Fig. 5(c)), data could only be measured to within $(T_M - T_C)/T_C \sim 0.1$ of the transition temperature $T_C$. The mean field model corresponding to long range order has theoretical values of $\beta=0.5$, $\gamma=1.0$ and $\delta=3.0$ while theoretical values based on the three dimensional Heisenberg model corresponding to short range interactions are $\beta=0.365$, $\gamma=1.386$ and $\delta=4.80$ [32]. The present results of $\beta = 0.77 \pm 0.12$, $\gamma = 1.09 \pm 0.07$ and $\delta = 2.51\pm0.06$, indicate that, even though there are mixed occupancies of Tb and Mn atoms and vacancies on the 8a site [9], long range interactions dominate the critical behaviour of TbNi$_2$Mn. This finding agrees with previous conclusions based on analyses of the Curie temperatures for the RNi$_2$Mn system (R=Tb, Dy, Ho, Er), that the magnetic ordering is dominated by the RKKY interaction between localized moments [9, 10]. However, the present exponent $\beta = 0.77$ compared with $\beta = 0.5$ for long range order is surprisingly large. $\beta = 0.57$ has been reported for single crystal Nd$_{0.7}$Sr$_{0.3}$MnO$_3$ [33] with this relatively high value ascribed to the formation of ferromagnetic clusters above $T_C$. According to Halder et al. [13], $\beta$ describes the rate of change of the ordered moment below $T_C$ with a smaller $\beta$ indicating more rapid the growth of the ordered moment. In the case of TbNi$_2$Mn, $\beta = 0.77$ indicates a slower growth of the ordered moment with decreasing temperature as is evident in the DC magnetic data (Fig. 3(a)). The slow growth of the ordered
moment in TbNi$_2$Mn is likely to be due to disorder of the local environments created by the presence of the mixing occupancy of Tb and Mn and vacancies at the 8a site [9].

3.3.2 Exponents - DC Field Magnetization

The variation of magnetization with applied DC field for TbNi$_2$Mn (102-186 K) and the resultant Arrot-plots of $M^2$ as a function of H/M are shown in Figs. 6(a) and 6(b) respectively. The Arrot-plots exhibit positive slopes as expected for the second order transition at $T_C$ [4]. The field dependence of magnetization for a second order system at $T_C$, can be expressed by equation (5) [17, 31] and provides a cross-check of exponent $\delta = 2.51 \pm 0.06$ derived from the DC field dependence of ac susceptibility:

\[ M \sim H^{1/\delta} \]  
(5).

The double-logarithmic M-H curves for TbNi$_2$Mn at 146 K and 150 K (Fig. 6(c); temperatures just above and below $T_C$) are well described by the power relation $M \sim H^{1/\delta}$ at both temperatures with linear fits leading to the values $\delta = 2.66 \pm 0.01$ and $\delta = 2.41 \pm 0.01$ respectively. As indicated in [17] and [31], M-H curves well below $T_C$ show an upward curvature away from linearity (leading to a larger value of $\delta$), M-H curves well above $T_C$ exhibit a downward curvature (leading to a smaller $\delta$) while for temperatures close to $T_C$, the M-H curves show linear behaviour. On this basis the $\delta$ values derived at 146 K ($\delta = 2.66 \pm 0.01$) and 150 K ($\delta = 2.41 \pm 0.01$) indicate that the $\delta$ value at $T_C = 147.0 \pm 1.7$ K from the DC magnetization data would be very close to the value $\delta = 2.51 \pm 0.06$ derived from equation (5) and Fig 5(a) as based on the ac susceptibility data.

The modified Arrot-plots, $M^{1/\beta}$ as a function of $(H/M)^{1/\gamma}$, shown in Fig. 6(d) provide a cross-check of our critical exponent analyses. Using $\beta = 0.77 \pm 0.12$ and $\gamma = 1.09 \pm 0.07$ derived from the susceptibility data, these modified Arrot-plots exhibit isothermal curves which are parallel to a high degree for DC fields $\mu_0 H > 2$ T. The average slope is $905 \pm 10$ (emu/g)$^{1/\gamma+1/\beta}T^{-1/\gamma}$ with slopes of $892 \pm 14$ (emu/g)$^{1/\gamma+1/\beta}T^{-1/\gamma}$ at the lowest temperature 102 K ($\sim -1.4 \%$) and $917 \pm 9$ (emu/g)$^{1/\gamma+1/\beta}T^{-1/\gamma}$ at
the highest temperature, 186 K (~ +1.3 %). This analysis demonstrates that the critical exponent values determined for $\delta$, $\beta$ and $\gamma$ from the ac susceptibility data, also describe the DC magnetic behaviour.

### 3.4 Magnetocaloric Effect

Given that many Laves phase compounds exhibit large magnetocaloric effects (MCE) [34-36], we investigated the magnetic entropy change for TbNi$_2$Mn*. The isothermal entropy change $\Delta S_M$ for magnetic field change $\Delta H$ from $H = 0$ to $H$, was derived from the Maxwell relation [1, 37]:

$$\Delta S_M(T, H) = \mu_0 \int_0^H \left( \frac{\partial M}{\partial T} \right)_H dH .$$  (6).

The magnetic entropy curves $-\Delta S_M$ (Fig. 7(a)) exhibit broad peaks around $T_C$ (typical for a second order phase transition [1]) with maximum values of $-\Delta S_M \sim 1.9$ J/kg K and $-\Delta S_M \sim 3.0$ J/kg K for $\Delta \mu_0 H = 0$-3 T and $\Delta \mu_0 H = 0$-5 T respectively. By comparison, for TbNi$_2$ where a sharp MCE peak was found around $T_C = 37.5$ K, $-\Delta S_M \sim 14.5$ J/kg K for field change $\Delta \mu_0 H = 0$-5 T [3]. The local disorder created by the mixed occupancy of Tb and Mn at the 8a site and vacancies is likely to contribute to increased broadening of $-\Delta S_M$ for TbNi$_2$Mn, leading to the reduced value of $-\Delta S_M$ compared with TbNi$_2$.

Mean field theory predicts that $-\Delta S_M$ is proportional to $(\mu_0 H/T_C)^{2/3}$ at second order phase transitions [37, 38]. The linear fit to data in Fig. 7(b) demonstrates that the relationship $-\Delta S_M \propto (\mu_0 H/T)^{2/3}$ is valid around $T_C$, in agreement with the conclusion from magnetization measurements that the magnetism of TbNi$_2$Mn is governed by long range interactions.

### 3.5 Mössbauer spectroscopy

Examples of Mössbauer spectra and fits for the $^{57}$Fe-doped TbNi$_2$Mn sample over the temperature range 5-300 K are shown in Fig. 8. As outlined below the fits allow the average values of the
The hyperfine parameters of TbNi$_2$Mn($^{57}$Fe) to be determined above and below the transition temperature (Fig 9). In the paramagnetic region above $T_C \sim 147$ K the spectra indicate features consistent with quadrupolar effects while below $T_C$ the spectra exhibit magnetic hyperfine splitting. As Mn atoms enter both 8a and 16d sites in RNi$_2$Mn compounds [9-11], it is assumed that the dopant $^{57}$Fe atoms also enter these sites. Consistent with this two-site occupancy, the spectra above $T_C$ are found to be fitted best using two doublets $D_1$ and $D_2$ ($\chi^2 \sim 1.16$) rather than one doublet ($\chi^2 \sim 1.25$). The optimal fits to spectra above $T_C$ (Fig. 8(a)) have fractional areas $D_1\sim10(1)$ % and $D_2\sim90(2)$ %. Rietveld refinements of room temperature TbNi$_2$Mn x-ray diffraction patterns show that $\sim10.0(0.5)$ % of the transition metal atoms occupy the 8a site with $90.0(0.5)$ % in the 16d site [9]. We therefore identify doublet $D_1$ as representing the behaviour of the 8a site with $D_2$ representing the behaviour of the 16d sites.

The spectra below $T_C$ (Fig. 8) show magnetic hyperfine splitting. The magnetically split spectra were fitted assuming a distribution of hyperfine fields leading to the graph of average field values versus temperature shown in Fig. 9(a). As discussed below, we have also fitted the magnetic spectra using two or three sextets to approximate the possible site transition metal occupancies of the 16d and 8a sites for comparison with refinement results [9].

The average hyperfine field shown in Fig 9(a) results from contributions to the exchange interactions present in the Tb and transition metal (Ni, Mn) sublattices and correspondingly reflect the magnetic order in the Tb and (Ni, Mn) sublattices [11, 37, 38]. The spectra for magnetically split spectra would therefore be expected to be fitted using two sub-sextets to represent $^{57}$Fe atoms in the 8a and 16d sites. In practice, we found that at least three sub-sextets are needed to provide optimal fits for the spectra below the magnetic ordering temperature $T_C$. For analysis of the TbNi$_2$Mn($^{57}$Fe) spectra below $T_C$, we assume that the line width and isomer shift are the same for all three sub-sextets with the magnetic hyperfine field and quadrupole interaction allowed to vary.
As shown in Fig. 9(a), the average hyperfine field values derived from fits based on three sextets (half filled diamonds) agree well with the average values derived from the field distribution fit (open triangles). The spectral fits using three sextets are shown in Fig. 8 as they allow comparison with site occupancies of the transition metal atoms determined from the earlier X-ray diffraction refinements [9]. The fit to the 5 K spectrum of Fig 8 for example, is represented by three sub-spectral sextets: \( S_1 \) of largest hyperfine field \( B_{hf1} \) and fractional area \( A_1 \sim 40 \pm 6 \% \); \( S_2 \) of medium hyperfine field \( B_{hf2} \) with \( A_2 \sim 49 \pm 7 \% \) and \( S_3 \) of smallest hyperfine field \( B_{hf3} \) with \( A_3 \sim 11 \pm 3 \% \).

Following the transition metal occupancies of the 16d and 8a sites [9, 10], we conclude that sextets \( S_1 \) and \( S_2 \) of combined fractional area \( \sim 90 \% \), correspond to the contribution from \(^{57}\text{Fe} \) at 16d sites with the third sextet \( S_3 \) representing \(^{57}\text{Fe} \) located at the 8a site of fractional area \( \sim 10 \% \). The spectral fits are found to be consistent with our conclusion that the Mn(\(^{57}\text{Fe} \)) atoms occupy both 16d and 8a sites in RNi\(_2\)Mn.

It should be noted that similar behaviour has been found for RMn\(_2\) compounds (R=Tb, Dy, Ho) where two sub-spectra rather than a single sub-spectrum are required [39-41] even though there exists only one transition-metal crystallographic site for magnetic state spectra. In the case of DyMn\(_2\) it was reported that magnetic and non-magnetic Mn atoms coexist below the ordering temperature [39] (this behaviour is linked with the strong dependence of the magnetic state of the Mn atoms on the critical Mn-Mn distance \( d_{\text{Mn-Mn}} \sim 2.66 \) Å), whereas for TbMn\(_2\) and HoMn\(_2\) the Mössbauer spectra below the magnetic ordering temperatures were fitted using at least two sub-sextets which are related to the nearest neighbour environment of the Fe atoms and/or the direction of the easy axis of magnetization [40, 41].

Fig. 9(a) also shows a fit of the average magnetic hyperfine field values to equation (7) which incorporates a superposition of collective electron and spin-wave effects [42]:

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As outlined by Chattopadhyay et al. [42], the $T^{3/2}$ term is due to excitations of long wavelength spin waves and the $T^{5/2}$ term results from spin wave-spin wave interactions [43], with the $T^2$ term arising from Stoner band excitations [44]. The dashed line in Fig 9(a) represents the best fit to the average magnetic hyperfine field values leading to constants $b=1.16 \times 10^{-3}$ K$^{-3/2}$, $c=1.64 \times 10^{-5}$ K$^{-5/2}$ and $d=2.47 \times 10^{-4}$ K$^{-2}$. This fit shows that the $T^{3/2}$ term, and therefore spin waves interactions dominate, while the $T^2$ term indicates that Stoner-type interactions also contribute to the magnetic behaviour of TbNi$_2$Mn($^{57}$Fe) with this itinerant character probably linked with the band magnetism of Ni. This type of temperature dependent behaviour – dominant $T^{3/2}$ but with $T^2$ contributions - is similar to that reported for the Fe$_{1-x}$Co$_x$Si [42] and MnSi [45] systems but differs from that in the R$_2$Fe$_{17}$-based systems where $T^2$ dependence of the hyperfine field was obtained [46].

As shown in Fig. 9(b) the average value of the quadrupole interaction $\varepsilon \sim 0.26$ mm/s for TbNi$_2$Mn($^{57}$Fe) above $T_C$ (the quadrupole shift $\varepsilon = |\Delta|/2$ for quadrupole splitting $\Delta$ [6]) is similar to values reported for the RMn$_2$ system ($\varepsilon = 0.171$ mm/s and $\varepsilon = 0.127$ mm/s for GdMn$_2$ and YMn$_2$ respectively [47]). While the sign of the quadrupole interaction cannot be derived from fits to spectra in the paramagnetic state above $T_C$, the asymmetry in the magnetic splittings below $T_C$, particularly evident in the sub-spectral sextets $S_1$, $S_2$ and $S_3$ (Fig 8(a)), is consistent with a positive value for the quadrupole interaction $\varepsilon$. A positive $\varepsilon$ also accounts well for the asymmetry observed in the predominantly quadrupolar spectra around $T_C$.

The Debye temperature of TbNi$_2$Mn($^{57}$Fe) has been determined from the temperature dependence of the isomer shift $IS(T)$ shown in Fig 9(c). The isomer shift is given by [48, 49]:

\[
IS(T) = IS_o(T) + IS_{s02}(T) \tag{8}
\]
IS\(_0\)(T) represents the temperature dependence of the charge density at the probe nucleus which is generally weakly temperature dependent. The second term, IS\(_{SODS}\), the so-called second-order Doppler shift, can be described in terms of the Debye model for the phonon spectrum by,

\[
IS_{SODS}(T) = -\frac{3kT}{2mc^2} \left[ \frac{3\theta_D^2}{8T} + 3 \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} \frac{x^3}{e^{x} - 1} dx \right],
\]

(9)
m is the mass of the \(^{57}\)Fe nucleus, \(k\) Boltzmann’s constant, \(c\) the velocity of light and \(\tau = \theta_D/T\) the reduced temperature [46, 48, 49]. The Debye temperature \(\theta_D\) has been derived to be \(\theta_D = 200 \pm 20\) K on fitting the mean isomer shift data of Fig. 9(c) to equation (9). The present value for the Debye temperature is similar to the value of \(\theta_D = 188 \pm 5\) K reported by Jackson et al. [10] from specific heat measurements. The Debye temperature value of \(\theta_D \sim 200\) K for TbNi\(_2\)Mn is consistent with the difference in \(\theta_D\) values for TbNi\(_2\) (\(\theta_D = 264\) K) [50] and TbMn\(_2\) (\(\theta_D = 145\) K) [51] with the reduced value for TbMn\(_2\) compared with TbNi\(_2\) resulting in the intermediate value for TbNi\(_2\)Mn. Similar behaviour has also been found for ErNi\(_2\)Mn related system [18].

4 Conclusions

In summary, the MgCu\(_2\)-type Laves phase of space group Fd-3m can be formed for the TbNi\(_2\)Mn\(_x\) system with Mn compositions in the range \(0.9 \leq x \leq 1.10\). The variations of the lattice parameter \(a\) and the Curie temperature \(T_C\) of TbNi\(_2\)Mn\(_x\) with Mn composition show similar behaviours to \(x = 1.0\). This strong correlation between the lattice constant and the Curie temperature is due to the sensitive dependence of both the RKKY interaction between Tb moments [9] and the Mn-Mn interactions, on the distance between magnetic atoms. For a given set of preparation conditions, reported differences in \(T_C\) values for TbNi\(_2\)Mn\(_x\) (e.g. Table I) are due to the concentration, \(x\), of Mn atoms and chemical pressure effects related to the variation in the spacing between magnetic atoms. As demonstrated by the variation of transitions temperature with the de Gennes factor \(G_R\) (Figure 3(c)), the magnetic behaviour of RNi\(_2\) and RMn\(_2\) compounds is governed by R-R interactions whereas additional T-T and R-T contributions are present in RNi\(_2\)Mn. These additional T-T and R-T components in the...
magnetic energy terms for RNi$_2$Mn contribute to their increased values of magnetic ordering temperatures compared with corresponding RNi$_2$ and RMn$_2$ compounds. A strong magneto-structural coupling exists in this system as reflected by the dependence of the lattice constant $a$ and transition temperature $T_C$ on composition and our calculation of the change of $T_C$ with unit cell volume (using $dT_C/dP \sim -1.96$ K/GPa for TbNi$_2$Mn [10]).

The magnetic phase transition at $T_C = 147\pm 1.7$ K in TbNi$_2$Mn has been determined to be second order. DC magnetization curves (0 - 5 T; 102-186 K) and ac susceptibility curves (100-200 K) taken at DC magnetic fields in the range 0.5 – 8.0 T, have been analysed in detail based on the conventional static scaling law. The resultant three critical exponents of the second-order phase transition in TbNi$_2$Mn are $\beta = 0.77 \pm 0.12$, $\gamma = 1.09 \pm 0.07$ and $\delta = 2.51\pm 0.06$, indicating that long range ordering interactions dominate this system. The magnetic entropy change around $T_C$ has been found to be 3.0 J/kg K for a magnetic field change of 0 T to 5 T. The combined magnetic field and temperature dependence of the entropy (Fig 8(b)) is also consistent with long range interactions. The temperature dependence of the average magnetic hyperfine field values indicates that spin wave interactions dominate, with Stoner-type interactions also contributing to the overall magnetic behaviour. TbNi$_2$Mn has a Debye temperature $\theta_D = 200(20)$ K as determined from the temperature dependence of the mean isomer shift.

**Acknowledgements**

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References:


Table I Structure and magnetic transition temperatures of Tb$_{2}$Mn$_{x}$ compounds together with information on sample preparation.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure</th>
<th>Preparation conditions</th>
<th>Space group</th>
<th>Lattice parameter $a$ (Å)</th>
<th>$T_C$ (K)</th>
<th>Reference</th>
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<tbody>
<tr>
<td>TbNi$_2$Mn</td>
<td>MgCu$_2$ (C15)</td>
<td>Annealed at 750 °C for 7 days</td>
<td>$Fd-3m$</td>
<td>7.158 Å</td>
<td>131 K</td>
<td>[9]</td>
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<tr>
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<td>Annealed at 900 °C for 5 days</td>
<td>$Fd-3m$</td>
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<td>151 K</td>
<td>[10]</td>
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<tr>
<td>TbNi$_2$Mn</td>
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<td>Annealed at 870 °C for 7 days</td>
<td>$F-43m$</td>
<td>7.1842 Å</td>
<td>142 K</td>
<td>[11]</td>
</tr>
<tr>
<td>TbNi$_2$Mn$_x$</td>
<td>MgCu$_2$ (C15)</td>
<td>Annealed at 870 °C for 7 days</td>
<td>$Fd-3m$</td>
<td></td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>TbNi$_2$Mn$_x$</td>
<td>MgCu$_2$ (C15)</td>
<td>As prepared</td>
<td>$Fd-3m$</td>
<td>7.149 Å, 7.177 Å, 7.202 Å, 7.190 Å, 7.190 Å</td>
<td>144 K, 149 K, 150 K, 145 K, 141 K</td>
<td>Present work</td>
</tr>
<tr>
<td>TbNi$_2$Mn*</td>
<td>MgCu$_2$ (C15)</td>
<td>As prepared</td>
<td>$Fd-3m$</td>
<td>7.178 Å</td>
<td>147 K</td>
<td>Present work</td>
</tr>
</tbody>
</table>
Figure Captions

Fig. 1 (a) X-ray diffraction patterns for as prepared TbNi$_2$Mn$_x$ samples with x=0.90, 0.97, 1.0, 1.03 and 1.10.
(b) Room temperature neutron diffraction pattern of the as prepared TbNi$_2$Mn* sample ($\lambda = 2.4072$ Å). The full line through the data corresponds to the Rietveld refinement with the residuals line also shown. The Bragg peak positions are indicated by the markers.

Fig 2 (a) Variation of the lattice constant $a$ with Mn composition for as-prepared TbNi$_2$Mn$_x$.
(b) Variation of the Curie temperature $T_C$, with Mn composition. $T_C$ was derived from the minimum in the $dM/dT$ versus T curve e.g. Fig 3(a).

Fig. 3 (a) Cooling and warming curves of the DC magnetization for TbNi$_2$Mn* ($\mu_0H_{DC}$=0.005 T).
The warming data were measured after first cooling in zero field (ZFC); the cooling data were then measured in the magnetic field (FC). The warming and cooling directions are indicated by the arrows with the Curie temperature marked for each sample. The $dM/dT$ versus T curve as derived from the cooling data is shown in the inset.
(b) Temperature dependence of the ac susceptibility on warming for TbNi$_2$Mn* ($\mu_0H_{DC}$=0.01 T) with the $d\chi/dT$ data shown as the inset.
(c) The magnetic ordering temperatures $T_C$ as a function of the de Gennes factor, $G_R=(g-1)^2J(J+1)$ for RNi$_2$Mn, RNi$_2$ and RMn$_2$ compounds (adapted from Fig 4 [9]). The dashed lines represent linear fits for RNi$_2$Mn ($T_C=9.89\times G_R+26.6$), RNi$_2$ ($T_C=3.39\times G_R$) and RMn$_2$ ($T_C=5.14\times G_R$).

Fig. 4 Temperature dependence of the ac magnetic susceptibility as measured in the DC magnetic fields indicated ($\mu_0H_{DC} = 0.5$ T to 8 T) for TbNi$_2$Mn*. The dashed line shows the locus of $T_M$, the temperatures of maximum susceptibility in the $\chi'_m(H, T)$ curves.
Fig. 5 (a) Values of $\chi_M$, the maxima in susceptibility for the different DC field values (0.5 T < $\mu_0H$ < 8 T), plotted against DC field on a double-logarithmic scale. The line represents a fit to the power law of equation (2).

(b) $T_M$, the temperature at which the maxima in susceptibility occurs in Fig. 4 plotted against $H^{1/(\gamma+\beta)}$, where $1/(\gamma+\beta) = 0.57$ are exponents based on the Heisenberg model. The zero field intercept yield a value of $T_C=147.0 \pm 1.7$ K.

(c) Values of $\chi_M$ plotted against the reduced temperature $(T_M-T_C)/T_C$ on a double-logarithmic scale. The line represents a fit to the power law of equation (3).

(d) Values of the reduced peak temperature $(T_M-T_C)/T_C$ plotted against the DC field on a double-logarithmic scale. The value of $T_C$ was determined as indicated in Fig. 5(b). The line represents a fit to the power law of equation (4).

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Fig. 6 (Colour online) (a) Magnetization as a function of applied DC field ($\mu_0H = 0 - 5T$) for TbNi$_2$Mn* around the Curie temperature $T_C$.

(b) Arrot-plots of $M^2$ as a function of $\mu_0H/M$ for the magnetisation data of Fig 6(a). The positive slopes indicate that the transition at $T_C$ is second-order.

(c) Magnetisation for TbNi$_2$Mn* at $T = 146$ K and $T = 150$ K versus DC field plotted on a double-logarithmic scale. The lines represents fits of $M$ versus $H$ resulting with $\delta = 2.66 \pm 0.01$ at 146 K and $\delta = 2.41 \pm 0.01$ at 150 K based on $M-H^{1/\delta}$, equation (5).

(d) Modified Arrot-plots of $M^{1/\beta}$ as a function of $(H/M)^{1/\gamma}$ for $\gamma =1.09$ and $\beta =0.77$ (exponents derived from fits to equations (3) and (4) in Figs 5(c) and (d) respectively).

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Fig. 7 (Color online) (a) Temperature dependence of the isothermal magnetic entropy change $-\Delta S_M(T, H)$ for TbNi$_2$Mn* as measured in magnetic fields up to 5 T and derived from equation (6).
(b) Dependence of the entropy change $-\Delta S_M(T,H)$ on the parameter $(\mu_0 H/T_C)^{2/3}$. The full line represents a linear fit to the data.

Fig. 8 (Color online) $^{57}$Fe Mössbauer spectra of TbNi$_2$Mn($^{57}$Fe) over the temperature range 5–300 K. As discussed in the text, the spectra above $T_C \sim 147$ K were fitted with two doublets ($D_1$ dashed line; $D_2$ dotted line) while the magnetic spectra below $T_C$ were fitted using three sextets ($S_1$- largest hyperfine field $B_{hf1}$, dash-dot line; $S_2$ - medium hyperfine field $B_{hf2}$; dotted line; $S_3$ - smallest hyperfine field $B_{hf3}$; dashed line).

Fig. 9 (Color online) Temperature dependences of the Mössbauer hyperfine parameters of TbNi$_2$Mn($^{57}$Fe) derived from the fits to the spectra shown in Fig 8.

(a) The average hyperfine field values $\langle B_{hf}\rangle$ determined using a distribution of hyperfine fields (open triangles) and three sextets (half filled diamond). As discussed in the text, the dashed line represents the best fit to the equation: $B_{hf}(T)=B_{hf}(0)(1+bT^{3/2}+cT^{5/2}+dT^2)$.

(b) The average quadrupole shift of the two sub-spectral components used to fit spectra above $T_C$ and the average quadrupole interaction values of the three sub-spectral components below $T_C$. The line is a guide to the eye.

(c) The mean isomer shift values; the dashed line represents the best fit to equation (8) resulting in the Debye temperature $\theta_D=200\pm20$ K.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
\[ \delta = 2.51 \pm 0.06 \]

\[ \gamma = 1.09 \pm 0.07 \]

\[ \gamma + \beta = 1.86 \pm 0.12 \]

\[ T_C = 147 \pm 1.7 \text{ K} \]

Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 9